

# Coulomb interactions of massless Dirac fermions in graphene; pair-distribution functions and exchange-driven spin-polarized phases.

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The quasi-2D electrons in graphene behave as massless fermions obeying a Dirac-Weyl equation in the low-energy regime near the two Fermi points. The stability of spin-polarized phases (SPP) in graphene is considered. The exchange energy is evaluated from the analytic pair-distribution functions, and the correlation energies are estimated via a closely similar four-component 2D electron fluid which has been investigated previously. SPPs appear for sufficiently high doping, when the exchange energy alone is considered. However, the inclusion of correlations is found to *suppress* the spin-phase transition in ideal graphene.

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*Introduction*— The carbon atoms in graphene form a quasi-two-dimensional (Q2D) honeycomb lattice and contribute one electron per carbon to form an unusual 2D electron system (2DES) with a massless Dirac-fermion dispersion near the Fermi points[1, 2]. Graphene and related materials (e.g, nanotubes, fullerenes) have become a mine of novel technologies and a new paradigm for studying various aspects of physics[3], including cosmological models on honeycomb branes, superconductivity on bi-partite lattices[4] and nanotubes[5], Hubbard models[6], spin-phase transitions[8], and other aspects of strongly correlated electrons[9].

The hexagonal Brillouin zone has two inequivalent points  $\mathbf{K}=(1/3, 1/\sqrt{3})$  and  $\mathbf{K}'=(-1/3, 1/\sqrt{3})$ , in units of  $2\pi/a_0$ , where  $a_0$  is the lattice constant. The simplest tight-binding model with nearest-neighbour hopping  $t$  is sufficient to describe the low-energy regime where the valence and conduction bands ( $\pi$  and  $\pi^*$ ) have linear dispersion near the  $\mathbf{K}$ ,  $\mathbf{K}'$  points, with zero bandgap. The graphene 2D electron system (G2DES) is nominally “half-filled”, with the  $\pi^*$  band unoccupied, and has spin and valley degeneracies, with a Berry phase associated with the valley index[2].

The vanishing of the density of states and the effective mass of the 2D electrons near the Fermi points suggest that the Coulomb interactions of the massless fermions remain strong, unlike in the usual Fermi-liquid picture. This also means that perturbation approaches have to be treated with great caution. The Coulomb interactions may induce a gap between the  $\pi$  and  $\pi^*$  bands, or a lifting of the sublattice (valley) degeneracies, or stabilize spin-polarized phases (SPP) in preference to the unpolarized state. Such SPPs in GaAs/AlAs 2DES, predicted to appear at low coupling ( $\sim 2 - 4$ ) when perturbation methods are used, get pushed to high coupling if non-perturbative approaches were used ( $\sim 26$ ), as discussed in Refs. [10, 11, 12]. The two-valley 2D electron system (2v-2DES) does *not* show a SPP when full non-

local non-perturbative calculations are used, presumably because these methods properly account for the direct interactions which are three times as many as the exchange interactions[12]. The exchange and correlation energy  $E_{xc}$  in the 2v-2DES of the Si/SiO<sub>2</sub> system was calculated from the distribution functions in Ref. [12], using the classical-map hyper-netted-chain (CHNC) technique, accurately recovering the Quantum Monte-Carlo (QMC) results even in the strong coupling regimes[13]. CHNC provides the pair-distribution functions (PDFs)  $g_{ij}(r)$  as a function of the coupling strength. Then  $E_{xc}$  is evaluated via a coupling constant integration. The method has been successfully applied to a variety of problems including the 2DES[14], the 2v-2DES in Si-MOSFET devices[12], and the thick quasi-2DES in HIGFET structures[16]. However, a direct calculation of exchange and correlation in graphene involves an  $8 \times 8$  matrix of two-component PDFs due to the spin and valley indices as well as the presence of  $\pi$ ,  $\pi^*$  bands. Hence in this study we consider the exchange energy  $E_x$  via an analytic evaluation of the non-interacting PDFs, and indirectly estimate the correlation energy  $E_c$  using results for the spin-polarized four-component 2v-2DES, exploiting the analogies between the two systems.

The non-interacting PDFs of G2DES, viz.,  $\mathcal{G}_{ij}^0(r)$  involve two components, the first being a Bessel function as in the ordinary 2DES, while a second, associated with the cosine of the angle of e-e scattering, involves Bessel and Struve functions, as we show below. We find that there are stable SPPs in an exchange-only approach. However, including the correlation energy using the 2v-2DES data stabilizes the *disorder-free* G2DES in the unpolarized state.

*Model for the graphene 2DES*—The kinetic energy near the  $\mathbf{K}$  points is given by a Dirac-Weyl Hamiltonian of the form:

$$H_k = v_F(p_x \tau_z \sigma_x + p_y \sigma_y) \quad (1)$$

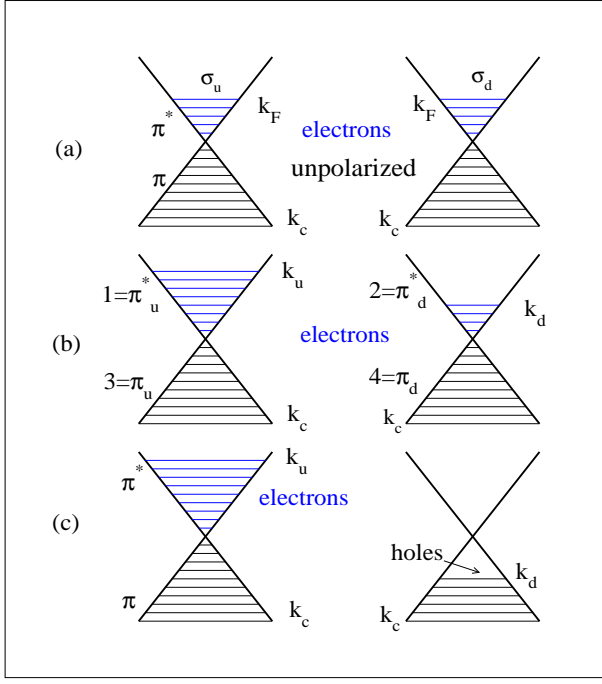


FIG. 1: (Color online) Linear dispersion bands near a  $\mathbf{K}$  point where the  $\pi^*$  and  $\pi$  bands cross. In (a) we show a doped unpolarized system with equal occupation of the up-spin ( $\sigma_u$ ) and down-spin states. In (b) the polarized system has only electron carriers. In (c) both electron and hole carriers occur. This is the only possibility if doping is zero ( $k_F = 0$  and  $k_u = k_d$ ).

Here  $\tau_z = \pm 1$  defines the degenerate valleys, and  $\sigma_x, \sigma_y$  denote the  $x$  and  $y$  Pauli matrices that act in the space of the two atoms in each unit cell. The  $\pi, \pi^*$  bands of spin and valley degenerate states (Fig. 1) show a linear dispersion  $E = \pm v_F \hbar k$ . This form requires a cutoff momentum  $K_c$  such that the number of states in the Brillouin zone is conserved. That is, if  $A_0$  is the area per carbon, then  $K_c^2 = 4\pi(1/A_0)$ . The electron density  $N_c$  at half-filling is  $1/A_0$ , with  $A_0 = a_0^2\sqrt{3}/2$ , since one  $\pi$  electron of arbitrary spin is provided by each carbon atom. The Fermi velocity  $v_F = \tau a_0\sqrt{3}/2$  is thus the slope of the linear dispersion, with  $v_F \sim 5.5$  eVÅ. If the G2DES is embedded in a medium with dielectric constant  $\epsilon_0$ , then we define

$$g^0 = \frac{e^2/\epsilon_0}{\hbar v_F} = \frac{e^2}{\epsilon_0 a_0} / (t\sqrt{3}/2). \quad (2)$$

This is the ratio of a typical Coulomb energy to the hopping energy and hence is usually taken as the Coulomb coupling constant of the G2DES. This plays the same role as the  $r_s$  parameter in electron-gas theory of nonrelativistic finite-mass fermions. The usual  $r_s$  is not available for G2DES since the effective mass  $m^*$  is zero and there is no effective Bohr radius. The coupling constant  $g^0$  is *maximized* if  $\epsilon_0$  is unity, and consistent with this case we assume  $g^0 = 2.75$  for our G2DES studies, and do not treat it as tunable.

The 4-component envelope-eigenfunctions of the kinetic energy term are made up of two-component functions  $U = (b, e^{i\phi_k})$ ,  $U' = (e^{i\phi_k}, b)$  and  $O = (0, 0)$  where  $\phi_k$  is the angle of the vector  $\vec{k}$  in the 2-D plane. Thus

$$F_{b,\vec{k}}^{\mathbf{K}}(r) = (2A)^{1/2}(U, O)_T \chi_\sigma \quad (3)$$

$$F_{b,\vec{k}}^{\mathbf{K}'}(r) = (2A)^{1/2}(O, U')_T \chi_\sigma \quad (4)$$

Here  $b = \pm 1$  is a  $\pi^*, \pi$  band index,  $(\cdots)_T$  indicates the transpose, and  $\chi_\sigma$  is the spin function. Then, using  $v = 1, 2$  as a valley index, the Coulomb interaction may be written in the form:

$$H_I = \frac{1}{8A} \sum_{v_i, b_i, \sigma_i} \sum_{\mathbf{k}, \mathbf{p}, \mathbf{q}} V_q \left[ b_1 b_4 e^{i\{\phi^*(\mathbf{k}) - \phi(\mathbf{k}+\mathbf{q})\}} + 1 \right] \times \left[ b_2 b_3 e^{i\{\phi^*(\mathbf{p}) - \phi(\mathbf{p}+\mathbf{q})\}} + 1 \right] \times a_{\mathbf{k}, v_1, b_1, \sigma_1}^+ a_{\mathbf{p}+\mathbf{q}, v_2, b_2, \sigma_2}^+ a_{\mathbf{p}, v_2, b_3, \sigma_2} a_{\mathbf{k}+\mathbf{q}, v_1, b_4, \sigma_2} \quad (5)$$

Here  $a^+, a$  are electron creation and annihilation operators and  $V_q = 2\pi e^2/(\epsilon_0 q)$  is the 2D Coulomb interaction. The phase factors introduce a novel  $\cos(\theta)$  contribution where  $\theta$  is the scattering angle, not found in the usual jellium-2DES. The resulting form of the exchange energy per Carbon is:

$$E_x/E_u = -\frac{A_0 g^0/k_c}{(2\pi)^2} \frac{1}{4} \sum_{b_1, b_2, \sigma} \int_0^{2\pi} d\theta dk dp \times kp \frac{1 + b_1 b_2 \cos(\theta)}{|\mathbf{k} - \mathbf{p}|} n_{b_1, \sigma}(k) n_{b_2, \sigma}(p) \quad (6)$$

Here we have introduced the intrinsic coupling constant  $g^0$  and the energy unit  $E_u = v_F k_c$ . Here  $k_c = K_c/\sqrt{2} = \sqrt{(4\pi n_c)}$  is based on the electron density per spin species,  $n_c = N_c/2 = 1/(2A_0)$ . The above form of the exchange energy can be reduced to an evaluation of a few elliptic integrals[8]. The normal “half-filled” G2DES can be doped with electrons or holes; but it is easy to show that symmetry enables us to limit to one type of doping. However, given a system with an areal density of  $N_\delta$  dopant electrons per valley, with  $n_\delta = N_\delta/2$  per spin, the carriers in the spin-polarized system could be electrons only, or both electrons and holes, as shown in Fig. 1 for the  $\pi^*$  and  $\pi$  bands at one  $\mathbf{K}$  point. The intrinsic system with  $n_\delta = 0$  can be an unpolarized state, as in Fig. 1(a), or spin-polarized state with electrons *and* holes, as in Fig. 1(c). Such exchange-driven systems have been studied by Peres et al.[8], while the correlation effects have not been considered. Since the correlation energy terms out-number the exchange terms by 3:1, it is imperative to include the correlation energies. The calculation of correlation energies is always more difficult than exchange energies. Peres et al. treated  $g^0$  as an externally tunable parameter for forcing SPPs. Here we evaluate the exchange energy  $E_x$  at the intrinsic  $g^0$ , from the non-interacting PDFs, and indirectly evaluate the correlation

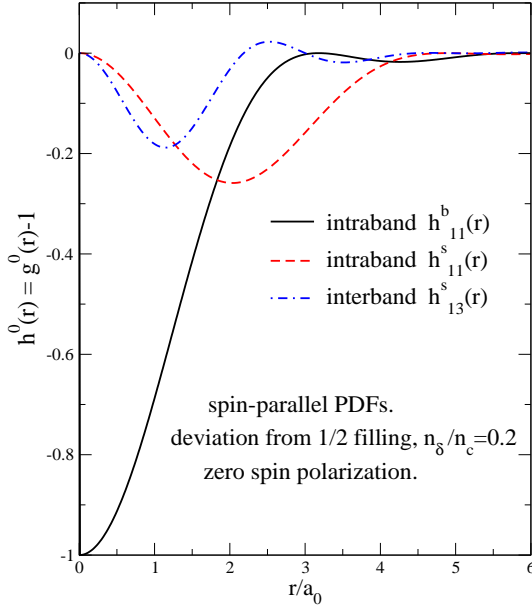


FIG. 2: (Color online) The Bessel-like and Struve-like non-interacting, parallel-spin PCFs  $h^b(r)$  and  $h^s(r)$  for the unpolarized doped system. The bands are numbered as in Fig. 1(b). The anti-parallel non-interacting PCFs are zero.

energy  $E_c$  from the four-component 2v-2DES with the same coupling strength ( $r_s = g^0$ ) and spin-polarization.

*Pair-distribution functions of the G2DES*— Although we are dealing with a four-component system (2-valleys, 2-spin states), as seen from Fig. 1, we need to consider the redistribution of electrons and holes among the  $\pi^*$  and  $\pi$  bands when comparing the energy of spin-polarized states with the unpolarized state. From Fig. 1 we see that the e-e interactions at a given valley can be constructed from (i) interactions with a  $\pi^*\sigma_u$  band of up-spin electrons of density  $n_u$ , filled to  $k_u$ , (ii) a  $\pi^*\sigma_d$  set of electrons or a  $\pi\sigma_d$  spin-down holes, of density  $n_d$ , filled up to  $k_d$  (iii) the  $\pi\sigma_u$  band, with electron density  $n_c$ , filled to  $k_c$  and (iv) the  $\pi\sigma_d$  band, density  $n_c$ , filled to  $k_c$ . There will also be similar inter-valley terms. Each term in this  $4 \times 4$  matrix, denoted by  $\mathcal{G}_{ij}(r)$  where  $i, j = 1 \dots 4$ , will have two components associated with those in  $U'$  and  $U = (b, e^{i\phi_k})$ . Thus  $\mathcal{G}_{ij}(r) = g_{ij}^b(r), g_{ij}^s(r)$ , where the superfixes “b, s” indicate that the noninteracting forms are Bessel-function like, and Struve-function like, respectively. The Struve form arises from the  $\cos(\theta)$  terms in the Coulomb interaction. The numbering scheme of the matrix is shown in Fig. 1(b). Thus, defining the pair-correlation functions (PCFs)  $\mathcal{H}_{ij}(r) = \mathcal{G}_{ij}(r) - 1$ , or its components  $h_{ij}(r) = g_{ij}(r) - 1$ , we have:

$$\begin{aligned} h_{ij}^{0,b}(r) &= -(n_i n_j)^{-1} \int_0^{k_i} \frac{d\mathbf{k}_1}{(2\pi)^2} \int_0^{k_j} \frac{d\mathbf{k}_2}{(2\pi)^2} e^{i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}} \\ &= -\frac{2}{k_i r} J_1(k_i r) \frac{2}{k_j r} J_1(k_j r) \end{aligned} \quad (7)$$

$$\begin{aligned} h_{ij}^{0,s}(r) &= -(n_i n_j)^{-1} \int_0^{k_i} \frac{d\mathbf{k}_1}{(2\pi)^2} \int_0^{k_j} \frac{d\mathbf{k}_2}{(2\pi)^2} \\ &\quad \cos(\theta_1 - \theta_2) e^{i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{r}} \\ &= -\frac{\pi}{k_i r} \frac{\pi}{k_j r} [J_0 H_1 - J_1 H_0]_i [J_0 H_1 - H_0 J_1]_j \end{aligned}$$

Here  $J_0, J_1$  are Bessel functions, while  $H_0$  and  $H_1$  are Struve  $H$ -functions. Also, in  $[J_0 H_1 - J_1 H_0]_i$  the functions are evaluated at the argument  $k_i r$ . The wavevectors  $k_i = \sqrt{4\pi n_i}$  are for each component  $i$ , of density  $n_i$ . We show typical noninteracting PCFs for a doped, unpolarized case as in, Fig. 1(a), with the doping fraction  $n_d/n_c = 0.2$ . In CHNC, the exchange-hole is mapped exactly into a classical Coulomb fluid using the Lado procedure[14]. The figure shows that the exchange-hole is strongly reduced by the presence of the  $\cos(\theta)$  term which has been averaged into the Struve-like PCFs  $h^s(r)$ . When the Coulomb interaction is included, the  $\cos(\theta)$  term has a similar mitigating effect and exchange-correlation in the G2DES is actually *considerably weaker* than in the corresponding 2v-2DES which may be realized in a Si MOSFET. The CHNC calculation for the 2v-2DES for the conditions stipulated in Fig. 2 show that the correlation energy is only about a third of the exchange energy at  $r_s = g^0$ . This and other model calculations allow us to conclude that a good approximation is to ignore the  $E_c$  contribution arising from the Struve-like distribution functions and estimate the  $E_c$  only from the Bessel-like functions which are the only forms appearing in the 2v-2DES. This justifies our use of the 2v-2DES for the correlation energy, while the  $E_x$  is exactly evaluated.

*The kinetic and exchange energies.*— When the doping per valley is  $N_d = 2n_d$ , the total number of electrons per valley is  $N_t = N_c + N_d$ . Also, using the  $i = 1, 2, 3, 4$  notation of Fig. 1(b), we set  $n_1 = n_u$ ,  $n_2 = n_d$ ,  $n_3 = n_4 = n_c$ . Hence the spin polarization  $s = n_u - n_d$ , where the band index  $b_d = -1$  for holes. The degree of spin-polarization  $\zeta = s/N_t$ . The composition fractions, inclusive of the valley index  $v = 1, 2$  are  $x_{vi} = n_i/2N_t$ . We note that  $k_F = \sqrt{2\pi n_d}$ ,  $k_u = \sqrt{2\pi(n_d + s)}$ ,  $k_d = \sqrt{2\pi(n_d - s)}$ . The exchange energy  $E_x(n_d, \zeta)$  can be written as:

$$\begin{aligned} E_x(n_d, \zeta)/N_t &= (N_t/2) \int \frac{2\pi r dr}{r} \\ &\times \sum_{ij} x_{vi} x_{vj} [\mathcal{G}_{v,v,ij}^0(r) - 1] \end{aligned} \quad (8)$$

It is implied that the Struve-like component in  $\mathcal{G}_{v,v,ij}$  where  $v$  label the valleys, is summed with the appropriate  $b_i b_j$  band  $\pm$  factors. Only a sum over the components in one valley is needed in evaluating the exchange. The calculation of both exchange and correlation involves exactly the same formula, but with a further integration over a coupling constant  $\lambda$  included in the PDFs  $\mathcal{G}_{v,v',ij,\lambda}$ . The above formula for  $E_x$  is made more explicit below. Thus, the total kinetic and exchange energy

$E_{kx} = K.E + E_x$ , for the case (b) of Fig. 1 can be written in terms of  $n_F, n_u, n_d$  and  $n_c$  as in Eq. 8, or in terms of  $k_F, k_u, k_d, k_c$  and  $A_0$  as:

$$E_{kx}(\zeta) = \frac{A_0}{6\pi} v_F (k_u^3 + k_d^3) - \frac{A_0}{(2\pi)^2} (g^0 v_F / 4) (\pi/2) [k_u^4 \mathcal{H}_{11}(r) + k_d^4 \mathcal{H}_{22}(r) + 2k_c^2 \{k_u^2 \mathcal{H}_{13}(r) + k_d^2 \mathcal{H}_{14}(r)\}] \quad (9)$$

The kinetic and exchange energy,  $E_{tx}(\zeta = 0)$  of the unpolarized system shown in Fig. 1(a), is obtained by setting  $k_F = 0$  when  $k_u = k_d$  in Eq. 9. The energy difference  $\Delta E_{kx}(\zeta)$  is plotted in the upper panel of Fig. 3. This equation reduces to Eq.(12)-(15) of Ref. [8] when the PDFs are replaced by their  $k$ -space forms and expressed in terms of elliptic integrals. We have done the calculations in  $r$ -space using PDFs, and in  $k$ -space via elliptic integrals, as a numerical check. The evaluations using elliptic integrals are numerically more stable. The results (Fig. 3) show that stable spin-polarized phases appear for systems containing purely electron carriers, when the dopant fraction  $f_d > 0.38$ .

*Effect of the correlation energy  $E_c$ .*— This requires the calculation of all the intra and inter-valley interacting PDFs of G2DES. Even using various symmetries, this involves calculating nearly two dozen PDFs as well as an integration over the coupling constant. We postpone this demanding task to future work. However, the  $E_c(n_\delta, \zeta)$  of G2DES may be quite well approximated from the closely analogous four-component 2v-2DES. This correlation energy/per electron,  $\epsilon(r_s, \zeta)$ , where  $r_s = g^0$ , is given in Eq. 5 of Ref. [12]. In transferring from the 2v-2DES to the G2DES we note that  $e^2/\epsilon_0$  which is unity in 2v-2DES becomes  $g^0 v_F$  in the G2DES. Also, the exchange term arising from the Bessel-like  $h_{11}(r)$ , and  $h_{22}(r)$ , calculated at the given coupling strength  $r_s = g^0$  and the spin polarization  $\zeta$  arise from the same PDFs in both systems. This establishes the scale factor connecting the energy units of the 2v-2DES and the G2DES at any given spin-polarization. Given the validity of Eq. 8, we adopt the same scale factor for converting the correlation energy  $E_c$  of the 2v-2DES to the G2DES. The energy difference  $\Delta E_{kxc}(\zeta)$ , inclusive of  $E_c$ , between the polarized and unpolarized phases calculated using the above approach is shown in the lower panel of Fig. 3. The exchange-driven SPP seems to be suppressed to within the uncertainty of this calculation of  $\Delta E_{kxc}$ . Improved estimates would only strengthen this calculation further.

In this work we have kept the Coulomb coupling fixed at  $g^0 = 2.75$  typical of graphene, unlike in other studies[6, 8] where the coupling strength  $g$  is taken as a tunable parameter, (in the spirit of Hubbard-model studies). Even in one-valley 2DES, the SPP of low-order theories is pushed to  $g \sim 26 - 27$ . In the 2v-2DES, direct terms (usually known as the correlation terms)

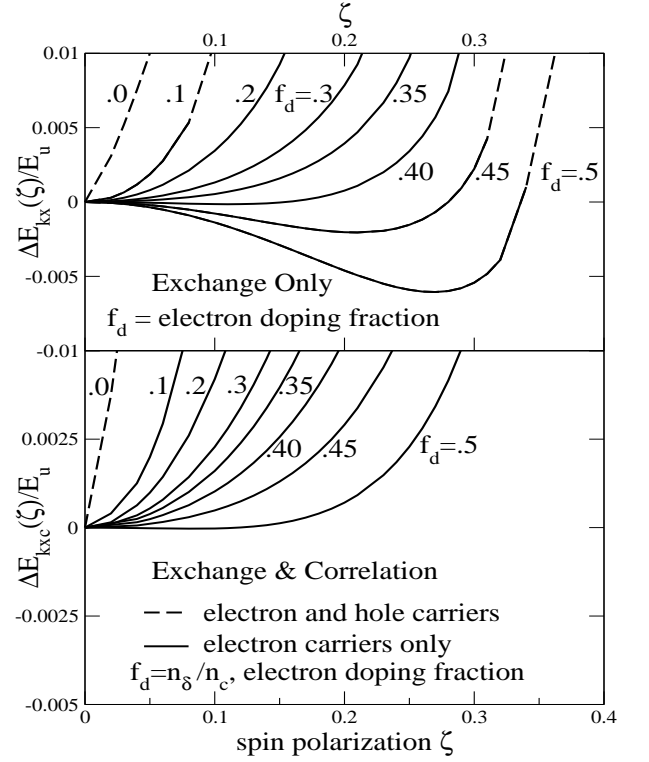


FIG. 3: Upper panel- the energy difference  $\Delta E_{kx}$ , i.e., K.E+exchange, between the polarized and unpolarized phases, in units of  $E_u = v_F k_c$ , as a function of the spin polarization  $\zeta$  and the dopant fraction  $f_d = n_\delta/n_c$ . Electron-carrier systems, Fig. 1(b) are more stable than electron-hole systems, and show stable spin-polarized states. However, addition of the correlation energy (lower panel) makes the unpolarized state the most stable phase.

predominate over exchange interactions, and the SPP is *suppressed*, as found in CHNC[12] or QMC[13]. Here too, we conclude that the inclusion of correlations *suppresses the exchange-driven spin-phase transition* in the ideal graphene system.

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